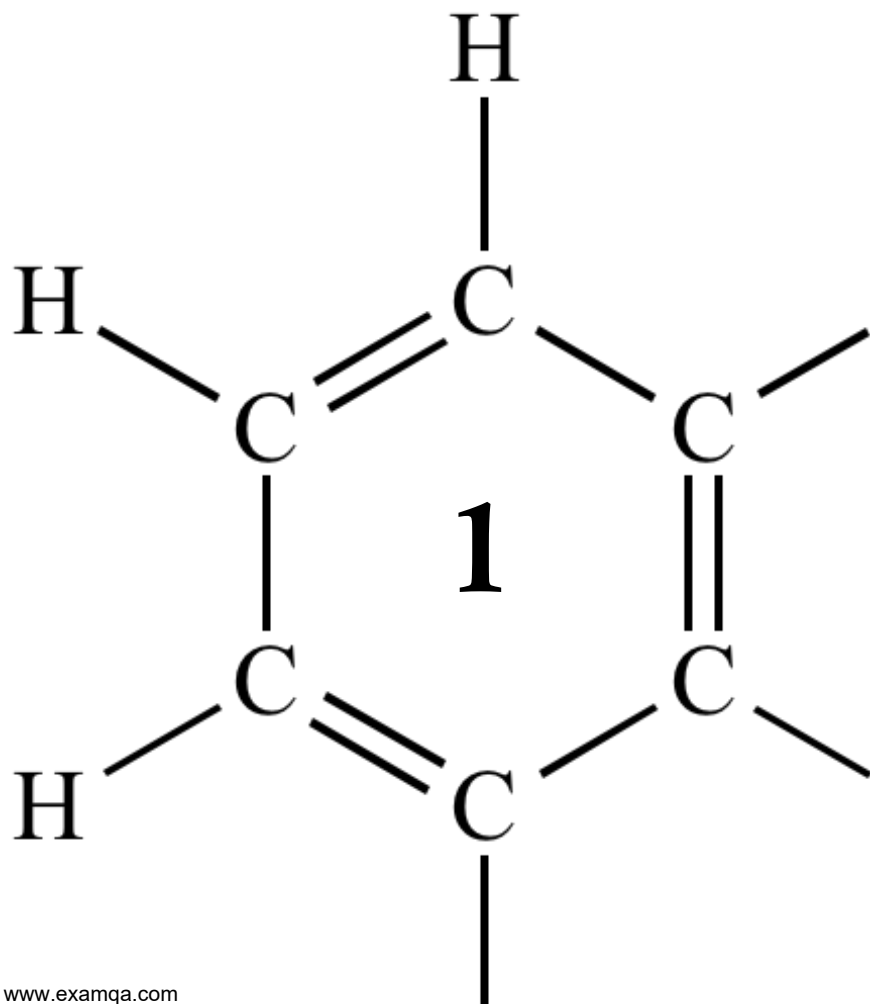


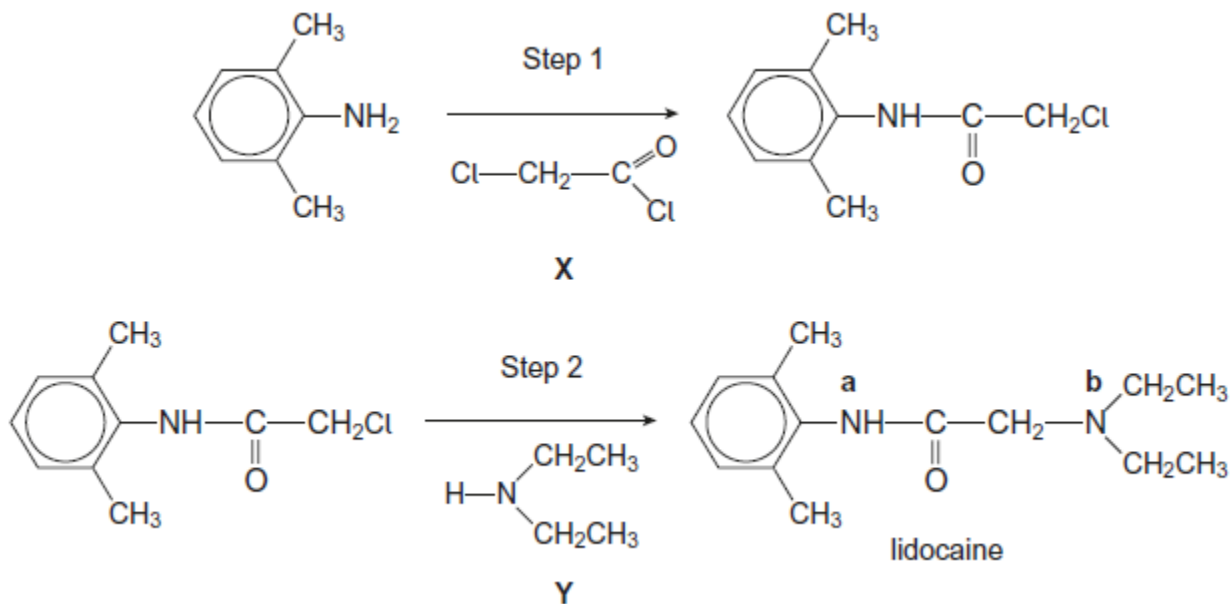
AQA A2 CHEMISTRY  
**SYNTHESIS ~ ANALYSIS**

N.M.R



1

Lidocaine is a local anaesthetic used in dentistry and in minor surgical operations. The synthesis of lidocaine in 2 steps from 2,6-dimethylphenylamine is shown.



- (a) (i) Give the IUPAC name of reagent **X** in Step 1.

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(1)

- (ii) Outline a mechanism for Step 1.  
In your answer, use  $\text{RNH}_2$  to represent 2,6-dimethylphenylamine.

(4)

- (b) Name the mechanism for Step 2.

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(1)

- (c) Which of these is the total number of peaks in the  $^{13}\text{C}$  n.m.r spectrum of lidocaine?

Tick (✓) one box.

8

9

11

12

(1)

(d) Calculate the percentage by mass of hydrogen in a molecule of lidocaine.

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(2)

(e) Give the name, including the classification, of the functional group that contains the nitrogen atom labelled **b**.

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(1)

(f) Lidocaine is used medically as the salt lidocaine hydrochloride.

(i) Suggest which one of the nitrogen atoms labelled **a** or **b** is protonated in lidocaine hydrochloride. Explain your answer.

Nitrogen atom protonated .....

Explanation .....

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(3)

(ii) Suggest why lidocaine hydrochloride is used medically in preference to lidocaine. Explain your answer.

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(2)

(Total 15 marks)

**2**

Compound **R** contains 61.0% carbon and 11.9% hydrogen by mass. The remainder is oxygen. The mass spectrum of **R** contains a molecular ion peak at  $m/z = 118$ .

(a) Use these data to show that the molecular formula of **R** is  $C_6H_{14}O_2$ .

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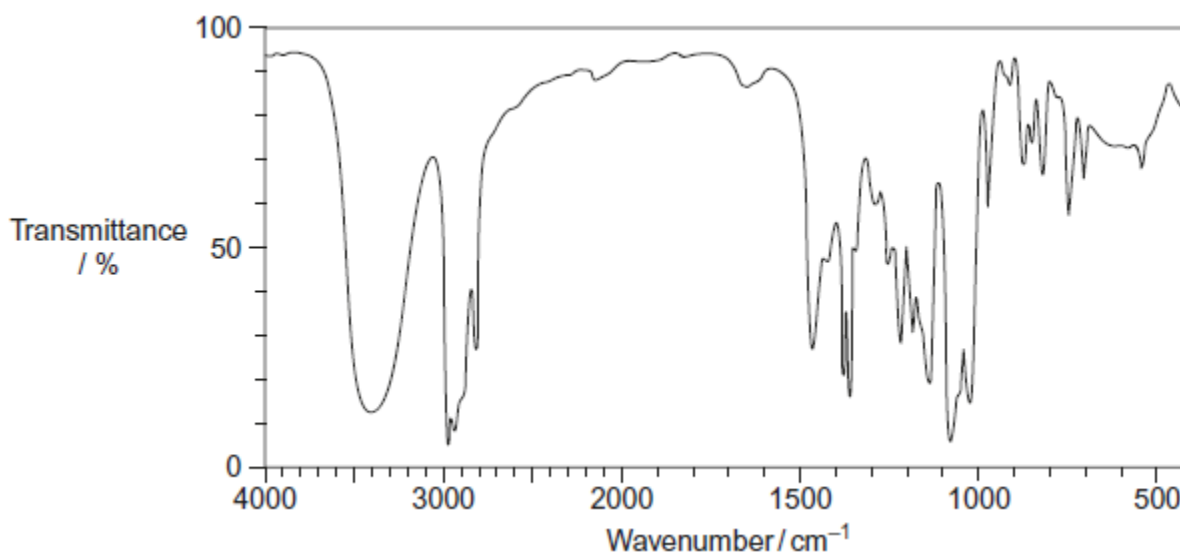
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**(3)**

(b) The infrared spectrum of **R** ( $C_6H_{14}O_2$ ) is shown below.



The proton n.m.r. spectrum of **R** contains five peaks. The chemical shift values, integration ratios and splitting patterns of these peaks are given in the table.

<b>Chemical shift/ppm</b>	3.8	3.2	3.1	1.4	1.1
<b>Integration ratio</b>	2	3	1	2	6
<b>Splitting patterns</b>	triplet	singlet	singlet	triplet	singlet

When **R** is warmed with acidified potassium dichromate(VI) a green solution is formed.

Use **Table A** and **Table B** on the data sheet and all of the data provided in the question to deduce the structure of **R**.

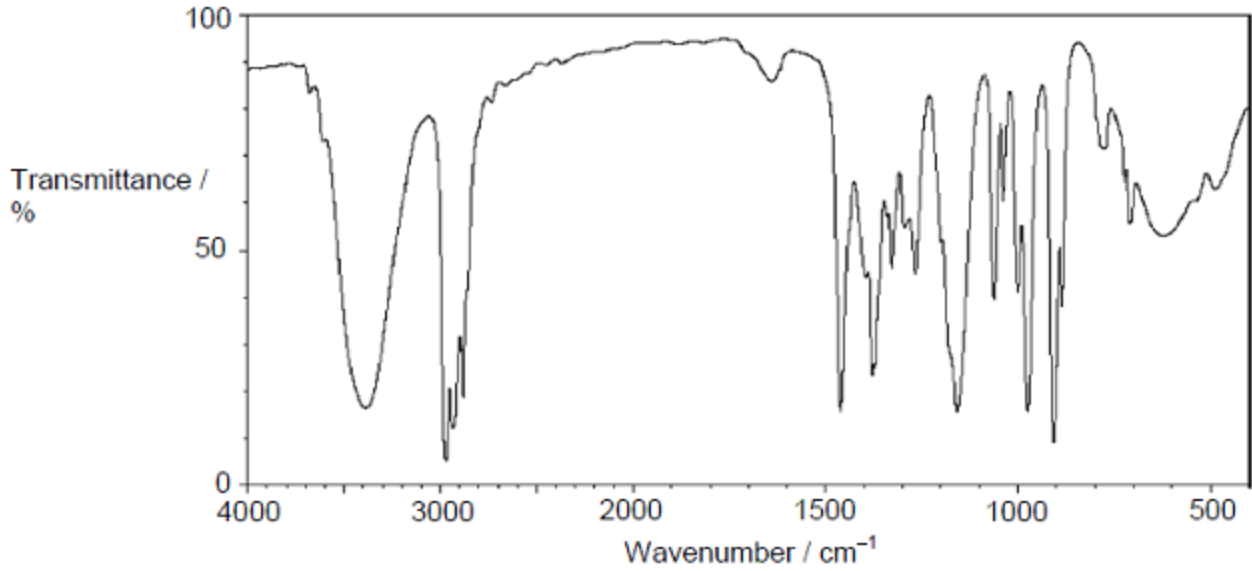
In your answer, explain how you have used the data provided in the question.

**(9)**  
**(Total 12 marks)**

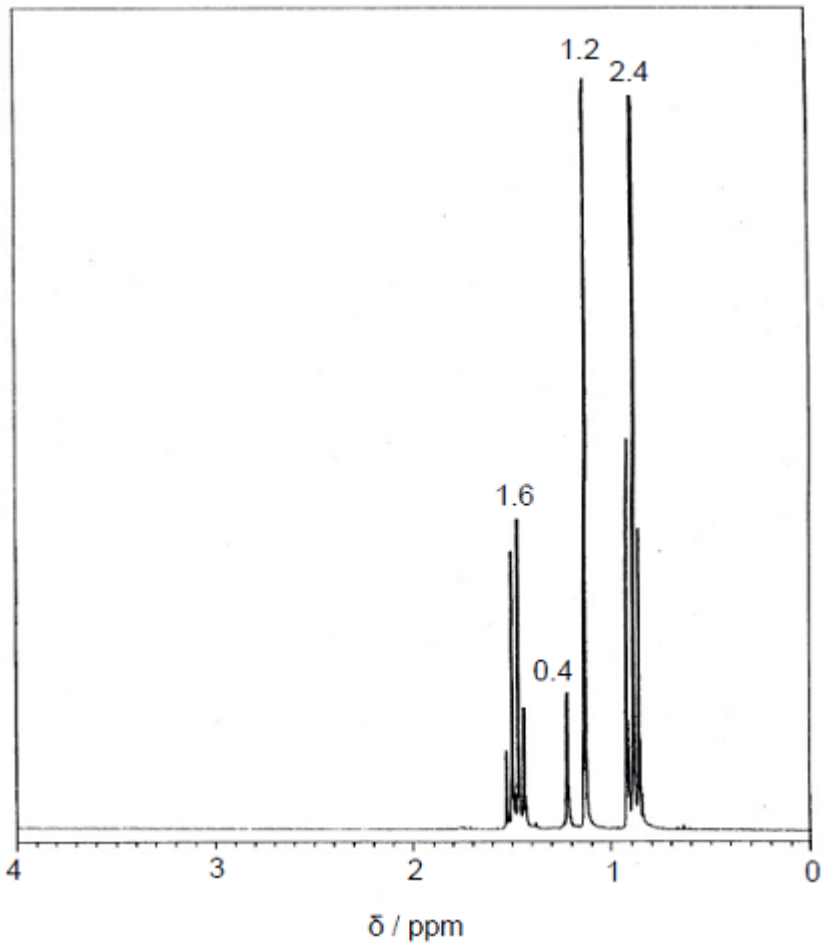
3

The infrared spectrum (**Figure 1**) and the  $^1\text{H}$  NMR spectrum (**Figure 2**) of compound **R** with molecular formula  $\text{C}_6\text{H}_{14}\text{O}$  are shown.

**Figure 1**



**Figure 2**



The relative integration values for the NMR peaks are shown on **Figure 2**.

Deduce the structure of compound **R** by analysing **Figure 1** and **Figure 2**.  
Explain each stage in your deductions.

Use **Table A** and **Table B** on the Data Sheet.

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(Total 8 marks)

4

Which amine has only **three** peaks in its proton NMR spectrum?

A Methylamine

B Trimethylamine

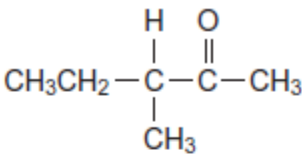
C Diethylamine

D Propylamine

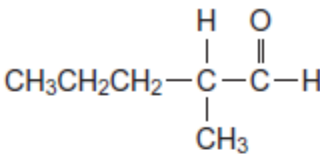
(Total 1 mark)

5

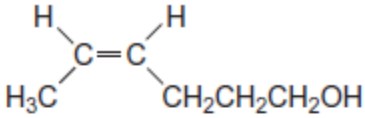
The following five isomers, **P**, **Q**, **R**, **S** and **T**, were investigated using test-tube reactions and also using n.m.r. spectroscopy.



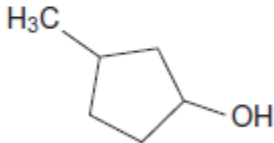
**P**



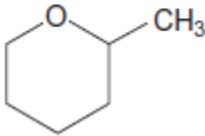
**Q**



**R**



**S**



**T**

(a) A simple test-tube reaction can be used to distinguish between isomers **P** and **S**.

Identify a reagent (or combination of reagents) you could use.  
State what you would observe when both isomers are tested separately with this reagent or combination of reagents.

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(3)

(b) A simple test-tube reaction can be used to distinguish between isomer **Q** and all the other isomers.

Identify a reagent (or combination of reagents) you could use.  
State what you would observe when **Q** is tested with this reagent or combination of reagents.

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(2)

(c) State which **one** of the isomers, **P**, **Q**, **R**, **S** and **T**, has the least number of peaks in its  $^1\text{H}$  n.m.r. spectrum.

Give the number of peaks for this isomer.

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(2)

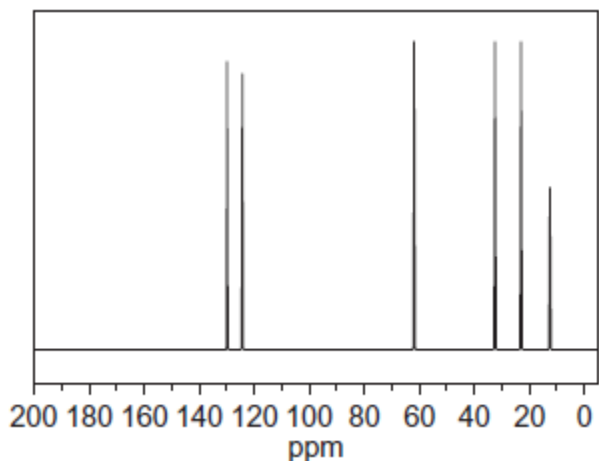
(d) Write the **molecular** formula of the standard used in  $^{13}\text{C}$  n.m.r. spectroscopy. Give **two** reasons why this compound is used.

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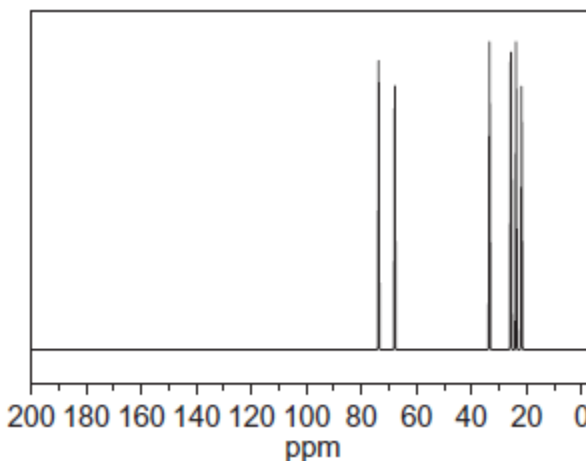
(3)

(e) **Figure 1** and **Figure 2** show the  $^{13}\text{C}$  n.m.r. spectra of two of the five isomers.

**Figure 1**

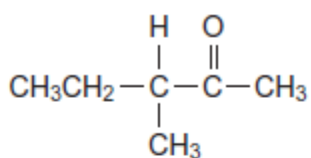


**Figure 2**

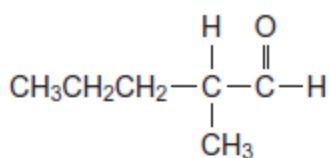




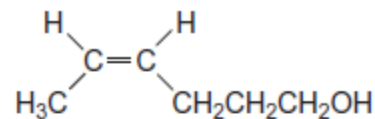
The structures of the five isomers are repeated to help you answer this question.



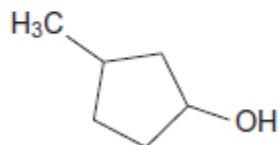
P



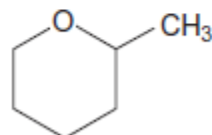
Q



R



S



T

State which isomer produces the spectrum in **Figure 1** and which isomer produces the spectrum in **Figure 2**.

Explain your answer.

You do not need to identify every peak in each spectrum.

Use **Table C** on the Data Sheet to answer the question.

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(5)

- (f) **U** and **V** are other isomers of **P**, **Q**, **R**, **S** and **T**.  
The  $^1\text{H}$  n.m.r. spectrum of **U** consists of two singlets.  
**V** is a cyclic alcohol that exists as optical isomers.

Draw the structure of **U** and the structure of **V**.

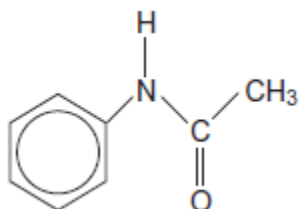
**U**

**V**

(2)  
(Total 17 marks)

6

The structure of N-phenylethanamide is



Use this structure to determine the number of peaks in the  $^{13}\text{C}$  n.m.r. spectrum of N-phenylethanamide.

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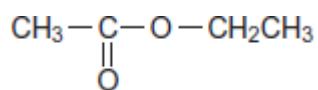
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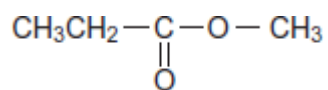
(Total 1 mark)

7

(a) Ester 1 and Ester 2 were studied by  $^1\text{H}$  n.m.r. spectroscopy.

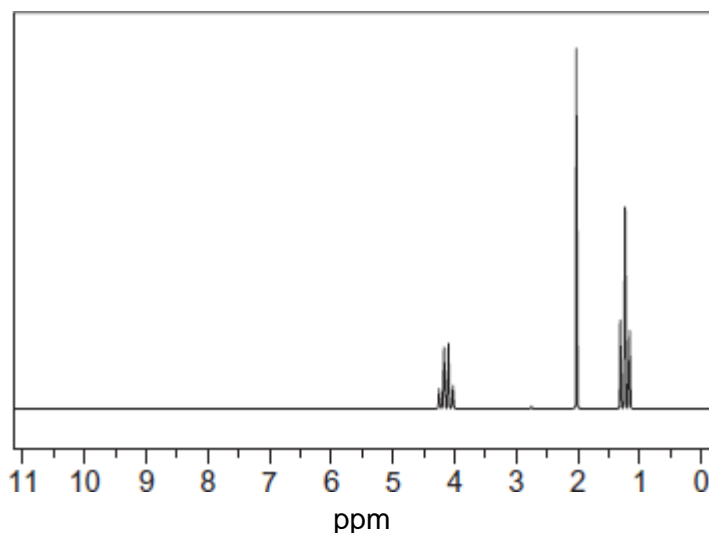


Ester 1



Ester 2

One of the two esters produced this spectrum.



Deduce which of the two esters produced the spectrum shown. In your answer, explain the position and splitting of the quartet peak at  $\delta = 4.1$  ppm in the spectrum.

Predict the  $\delta$  value of the quartet peak in the spectrum of the other ester.

Use **Table B** on the Data Sheet.

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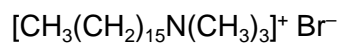
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(4)

(b) Cetrimide is used as an antiseptic.



cetrimide

Name this type of compound.

Give the reagent that must be added to  $\text{CH}_3(\text{CH}_2)_{15}\text{NH}_2$  to make cetrimide and state the reaction conditions.

Name the type of mechanism involved in this reaction.

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**(4)**

(c) Give a reagent that could be used in a test-tube reaction to distinguish between benzene and cyclohexene.

Describe what you would see when the reagent is added to each compound and the test tube is shaken.

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**(3)**

**(Total 11 marks)**





- (c) Draw the structure of each of the following isomers of  $C_5H_8O_2$   
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

**L** is methyl 2-methylpropenoate.

**M** is an ester that shows E-Z stereoisomerism.

**N** is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

**P** is an optically active carboxylic acid.

**Q** is a cyclic compound that contains a ketone group and has only two peaks in its  $^1H$  n.m.r. spectrum.

(5)  
(Total 19 marks)